

SURFACE WATER METABOLISM POTENTIAL OF GROUNDWATER-FED
NEAR SHORE WATERS ON THE LEEWARD COAST OF THE ISLAND OF
HAWAII

Presented to the Faculty of the
Tropical Conservation Biology and Environmental Science Graduate Program
University of Hawai`i at Hilo

In partial fulfillment of the requirement for the degree of
Master of Science
In
Tropical Conservation Biology and Environmental Science

By
Erik E. Johnson

Hilo Hawai`i
June 2012

UMI Number: 1518113

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent on the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI 1518113

Copyright 2012 by ProQuest LLC.

All rights reserved. This edition of the work is protected against unauthorized copying under Title 17, United States Code.



ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346

© Erik E. Johnson, 2012

SURFACE WATER METABOLISM POTENTIAL OF GROUNDWATER-FED
NEAR SHORE WATERS ON THE LEEWARD COAST OF THE ISLAND OF
HAWAII

By Erik E. Johnson

Approved by:

Dr. Tracy N. Wiegner, Chairperson
Dr. Jason E. Adolf, Committee member
Dr. Matthew J. Church, Committee member

May 14th, 2012

ACKNOWLEDGEMENTS

I would sincerely like to thank Gene, Patricia, Kristine, and Gwen for their continued support throughout my academic endeavors, and to whom this thesis is dedicated. I would also like to thank the rest of my family and friends whose support helped make this possible. It is with much gratitude that I thank my mentor, Tracy Wiegner, for her guidance, insight, and encouragement which helped shape this project and bring it to fruition.

This project would not have been possible without J. Adolf and M. Church whose guidance and comments helped improve this project. I would also like to thank J. Walker, R. Most, A. Bulseco, and N. Lindsey for assistance in sample collection and processing, and L. Mead for assistance with developing methods. This project was funded by National Science Foundation Grant No. EPS-0903833. Additional funding was provided by a research grant from the Partnerships for Reform in Math and Science (PRSIM) program. Any views, opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation (NSF) or any of its sub agencies.

ABSTRACT

Submarine groundwater discharge (SGD) has become increasingly recognized as an important source of freshwater and nutrients to coastal waters worldwide. Although groundwater nutrients have been found to cause algal blooms in many temperate coastal waters, little is known about the biological response to these nutrients in the tropics. On the leeward coast of Hawaii Island, SGD is the dominant freshwater and nutrient source to coastal waters. Kiholo Bay and Kaloko-Honokohau National Historical Park are two nearshore regions with well-documented SGD with high nutrient concentrations; however, little is known about how biological processes within the water column respond to these inputs. This study examined how gross primary production (GPP), respiration (RESP), and metabolism (MET) within surface waters differed inside and outside of groundwater plumes at these two sites and between wet and dry seasons. GPP and RESP were both significantly higher within groundwater plumes, suggesting that groundwater inputs stimulate these biological processes; however, RESP responded to a much greater extent than GPP, resulting in heterotrophic surface waters. Overall autotrophic conditions were found within groundwater plumes at Kiholo Bay, while heterotrophic conditions were found within groundwater plumes at Kaloko-Honokohau, indicating that the biologic response to SGD varies over short spatial and temporal scales.

KEYWORDS

Metabolism; primary production; respiration; submarine groundwater discharge

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	4
ABSTRACT	5
LIST OF TABLES.....	7
LIST OF FIGURES	8
LIST OF APPENDICES	9
INTRODUCTION	10
MATERIALS AND METHODS	13
RESULTS	18
DISCUSSION:.....	21
CONCLUSION.....	28
TABLES.	34
FIGURES.....	36
APPENDICES	42

LIST OF TABLES

Table 1: Physiochemical measurements of surface waters.....	33
Table 2: Biological measurements of surface waters.....	34

LIST OF FIGURES

Figure 1: Map of Kiholo Bay and Kaloko-Honokohau.....	35
Figure 2: Map of surface water salinity at Kiholo Bay and Kaloko-Honokohau.....	36
Figure 3: Mixing plot of nitrate + nitrite concentrations and salinity.....	37
Figure 4: Average GPP, RESP, and MET at Kiholo Bay and Kaloko-Honokohau.....	38
Figure 5: Regressions of GPP versus MET, RESP versus MET, and GPP versus RESP.....	39
Figure 6: Regressions of GPP versus phytoplankton biovolume and GPP versus nitrate + nitrite concentrations.....	40

LIST OF APPENDICES

Appendix A: Photosynthesis versus irradiance curves for Kiholo Bay and Kaloko- Honokohau.....	41
Appendix B: Regression analysis of the luminescence dissolved oxygen method versus Winkler titration method for determination of DO concentrations.....	42

INTRODUCTION

Groundwater discharge has become increasingly recognized as an important freshwater and nutrient source to coastal waters worldwide (Umezawa et al. 2002; Garrison et al. 2003; Slomp and Van Cappellen 2004; Hwang et al. 2005; Paytan et al. 2006). Nutrient loads from groundwater entering the coastal zone have been found to be a significant source of excess nitrogen and phosphorus that can rival and exceed that of riverine inputs in some regions and in some instances result in coastal eutrophication (Slomp and Van Cappellen 2004). Groundwater nutrient inputs have caused nuisance and harmful algal blooms in many coastal regions (Gobler and Sanudo-Wilhelmy 2001; Hu et al. 2006).

Quantifying how an ecosystem responds to water quality perturbations is crucial in evaluating the effects of coastal eutrophication. Ecosystem metabolism (MET) is an effective measurement that assesses the biological response of an ecosystem to environmental perturbations, such as excess nutrient and organic matter inputs (Smith and Hollibaugh 1993). MET measures the difference between gross primary production (GPP) and respiration (RESP), and is often measured to determine the trophic status of a water body. In net autotrophic systems, organic matter production from GPP exceeds consumption by RESP, resulting in an increase in pO_2 and a decrease in pCO_2 within the water body. In contrast, net heterotrophic systems have greater organic matter consumption than production, with a decrease in pO_2 and increase in pCO_2 , and are a net source of CO_2 to atmosphere. Additionally, MET can be used to describe trophic efficiency. In a tightly coupled system, RESP is almost entirely supported by GPP, and has a MET near zero. In a less efficient system, RESP may exceed GPP due to consumption of allochthonous organic matter.

There is high variability in coastal MET which can be attributed to factors influencing primary production and RESP. These factors can be physical, such as light levels (Cotner et al. 2000; Caffrey et al. 2007) and water temperature (Caffrey 2004), chemical, such as nutrient and organic matter loadings to coastal waters (D'Avanzo et al. 1996; Smith and Hollibaugh 1993, 1997), or biological, such as plankton biomass, plankton community composition, and trophic interactions such as grazing pressure and viral infections (Fuhrman 2000). Of these, the ratio of dissolved organic matter (DOM) to inorganic nutrient concentrations is thought to be one of the most influential parameters affecting MET (Kemp et al. 1997; Eyre and McKee 2002; Delgadillo-Hinojosa et al. 2008). A high ratio of DOM to nutrient concentrations generally promotes RESP over GPP, while a low ratio of DOM to nutrients tends to stimulate GPP over RESP. Allochthonous organic matter from rivers to estuaries is thought to drive estuarine RESP (Smith and Hollibaugh 1993; Delgadillo-Hinojosa et al. 2008; Thottathil et al. 2008); however, we presently do not know if the same is true for groundwater-fed coastal waters. In these systems, the amount of allochthonous DOM entering the coastal waters is low because it is removed within the vadose zone before entering the estuary (Slomp and Van Cappellen 2004), possibly leading to a lower DOM to nutrient ratio and potentially resulting in more autotrophic systems. Both groundwater and river inputs have strong seasonal variability, with higher flux of water and nutrient concentrations during wet seasons compared to dry seasons (Medina-Gómez and Herrera-Silveira 2006; Caffrey et al. 2007; Thottathil et al. 2008). Seasonal variations in these freshwater inputs leads to seasonal variation in MET in both temperate (Caffrey 2004) and tropical estuaries (Pradeep Ram et al. 2003; Thottathil et al. 2008), as inorganic nutrients, organic matter, and many other physiochemical parameters that influence both GPP and RESP vary with freshwater input.

Most studies examining GPP, RESP, and MET to date have focused on temperate estuaries (D'Avanzo et al. 1996; Kemp et al. 1997; Caffrey 2004, 2007; Delgadillo-Hinojosa et al. 2008), with few having been conducted in the tropics (Thottathil et al 2008; Mead and Wiegner 2010), especially in regions where groundwater is the prevalent freshwater input (Medina-Gómez and Herrera-Silveira 2006). The Hawaiian Islands are an ideal place to study the influence of groundwater inputs on the tropical coastal ocean. Groundwater discharge is especially important on the leeward coast of the Island of Hawaii, where the relatively young and permeable basalt limits the formation of streams and surface water runoff (Oki et al. 1999). Groundwater discharge has been found to be a significant source of nutrients to coral reefs on Hawaii Island's leeward side (Slomp and Van Cappellen 2004; Paytan et al. 2006; Street et al. 2008). On the Island of Maui, groundwater nutrients are responsible for large benthic macroalgal blooms, which have overgrown coral reefs and resulted in a considerable amount of ecological damage and economic losses in tourist revenue (Van Beukering and Cesar 2004; Smith and Smith 2006). While the effects of groundwater nutrients in Hawaii have been studied on macroalgae, the effects of these nutrients on microbes within the surface waters are not known.

The purpose of this study was to examine the biological response of coastal waters to groundwater nutrients at two sites on the leeward coast of Hawaii Island, where groundwater discharge is well documented (Knee et al. 2008; Peterson et al. 2009). Specifically, the response of GPP, RESP, MET, phytoplankton, and bacterial abundances within the surface waters to groundwater nutrient and organic matter inputs were examined. This study is novel in that it is one of the few that have examined MET in the tropics, and that was conducted in areas where freshwater inputs are dominated by groundwater discharge. This information is important as upland development, climate change, and invasive flora may be impacting the quality and

quantity of groundwater discharging into the coastal ocean, especially on the leeward side of Hawaii Island.

MATERIALS AND METHODS

STUDY SITE DESCRIPTION

The leeward coast of Hawaii Island is arid ($<25 \text{ cm y}^{-1}$); however, high rainfall ($>45 \text{ cm y}^{-1}$) on Hualalai, a 2,521-m basalt shield volcano, enters the coastal ocean through groundwater discharge (Peterson et al. 2009). Two coastal regions where groundwater inputs have been well documented are Kiholo Bay and Kaloko-Honokohau National Historical Park (Knee et al. 2008; Peterson et al. 2009) (Fig. 1). The Kiholo Bay watershed is 90.9 km^2 , which is largely undeveloped, with groundwater discharge rates estimated to be $7100 \text{ m}^3 \text{ d}^{-1}$ (Peterson et al. 2009). However, the surrounding *Prosopis pallida* (mesquite) trees, which host N_2 -fixing bacteria and are phreatophytic, may increase nitrogen concentrations within the groundwater, while reducing the amount of groundwater entering the nearshore waters. In contrast, the Kaloko-Honokohau National Historical Park watershed is a much smaller area (18.8 km^2), with groundwater discharge rates estimated to be $10 - 382 \text{ m}^3 \text{ d}^{-1}$ (Knee et al. 2008). Kaloko-Honokohau National Historical Park is threatened by upland development; its watershed is much more developed than Kiholo Bay's one, containing a wastewater treatment plant injection well, county landfill, and a golf course, as well as rapidly expanding residential and industrial areas (DeVerse 2006). Groundwater entering Kaloko-Honokohau National Historical Park has been characterized as having high nutrient concentrations (Johnson et al. 2008; Knee et al. 2008; Street et al. 2008); in comparison, nutrient inputs to Kiholo Bay are not well characterized.

SALINITY MAPPING

To delineate and determine extent of groundwater plumes, high-resolution spatial surface water salinity mapping was conducted by continuously pumping surface water (5- 10 cm deep) with an 800 L h⁻¹ impeller driven bilge pump through a YSI 6600V2 multi-parameter sonde interfaced with a YSI 650 MDS data logger and a Garmin etrex GPS unit. This setup (a modification of Bean et al. 2002) was mounted to a kayak, which was navigated around the coastline and then within that boundary in a grid-like fashion, while surface water salinity and GPS coordinates were recorded every three seconds. Data were uploaded through YSI's Ecowatch® software and imported into Golden Software's SURFER 9. High resolution maps of surface water salinity for each sampling event were developed using a Krigging interpolation. (Fig. 2).

WATER COLLECTION AND ANALYSES

To examine the influence of groundwater in the coastal ocean, surface water (<5 cm) samples were collected as groundwater and its constituents are separated from ocean water by density stratification. Surface water from each of the two sites was collected from six stations per sampling event, with three stations haphazardly chosen within the groundwater plume and three stations outside of it between March 2011 and February 2012. Wet and dry seasons were defined using the Hawaii Department of Health's delineations, where the wet season occurred from November to April and the dry season was from May to October. In- and out-plume stations were selected during surface water salinity mapping. Samples were collected at low tide when groundwater fluxes are most detectable (Peterson et al. 2009). Water samples were collected in

10-L acid-washed high-density polyethylene carboys, which were insulated with towels, away from direct sunlight to maintain a stable temperature (± 0.3 °C) during transport to the laboratory.

Water samples for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP), as well as for $\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} , H_4SiO_4 , and NH_4^+ were taken from each carboy, filtered through a combusted (6 h at 500 °C) GF/F (Whatman®) filter, and stored frozen until analysis. DOC and TDN were analyzed on a Shimadzu TOC-V CSH, TNM-1 analyzer following recommendations of Sharp et al. 2002 to provide detection limits (DL) of 10.0 and 5.0 $\mu\text{mol L}^{-1}$, respectively. Dissolved organic nitrogen (DON) was calculated from the differences between TDN and dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$). Concentrations of $\text{NO}_3^- + \text{NO}_2^-$ (USEPA 353.4, DL= 0.1 $\mu\text{mol L}^{-1}$), PO_4^{3-} (USEPA 365.5, DL= 0.1 $\mu\text{mol L}^{-1}$), H_4SiO_4 (USEPA 366, DL= 1.0 $\mu\text{mol L}^{-1}$), NH_4^+ (USGS I-2525, DL= 1.0 $\mu\text{mol L}^{-1}$), and TDP (USGS 4650-03, DL= 0.5 $\mu\text{mol L}^{-1}$) were determined using a Technicon Pulse II AutoAnalyzer. Dissolved organic phosphorous (DOP) was calculated from the difference between TDP and PO_4^{3-} . GF/F filters used here were then flash frozen and stored at -80°C until Chlorophyll *a* (Chl *a*) analysis. Chl *a* was measured on a Turner 10-AU fluorometer following EPA method 445.0. All inorganic and organic nutrient samples were analyzed at the University of Hawaii at Hilo Analytical Laboratory.

To quantify phytoplankton and bacterial abundances, water from each carboy was removed, combined with glutaraldehyde (for a final concentration of 0.5% glutaraldehyde), and placed on ice for 20 min before storage at -80°C. Thawed samples were analyzed on an Accuri C6 flow cytometer, calibrated with Invitrogen Countbrite® counting beads and Spherotech® 8-peak validation beads. Samples for phytoplankton analysis were analyzed for two min with a single wash and agitation between samples. For bacterial analysis, samples were stained with

Invitrogen SYTO BC green nucleic acid stain and analyzed for 20 s, with two washes between samples. Estimated spherical volume (ESV) of phytoplankton, calculated from size and abundance measurements derived from flow cytometry, was used as a proxy for phytoplankton biovolume (Li et al. 1993).

Physiochemical parameters were also measured from each carboy including: turbidity (Hach 2100P), pH (VWR sympHony SP70P), water temperature, and salinity (YSI 6600V2 sonde). Photosynthetically active radiation (PAR) was measured *in situ* using a Li-Cor LI-250A with a spherical quantum sensor.

O₂ INCUBATIONS

Changes in dissolved oxygen (DO) concentration were measured in light/dark bottle incubation experiments to determine GPP, RESP, and MET. Incubations were conducted under controlled laboratory conditions (and are referred to as potential measurements) in order to make comparisons over spatial and temporal scales as natural variations in light intensity and water temperature can strongly influence these processes. Each carboy was mixed and siphoned (overflowing three times) into eight, acid-washed, 60 ml Wheaton® borosilicate biological oxygen demand (BOD) bottles. Initial DO concentration was measured from each BOD bottle. Four bottles were incubated in the dark, while the remaining four were incubated at a light intensity of $460 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$, the intensity at which the highest rate of photosynthetic activity occurred, as determined through photosynthesis vs. irradiance curves for each site (Appendix A). The BOD bottles were incubated at 25°C (within 1°C of ambient site temperatures) in a cooler filled with sample water for 14 h to provide a measurable change in DO concentration in both light and dark treatments. DO concentrations were measured using a

Hach® LBOD101 luminescence DO probe (ASTM D888-05 method C), calibrated using the water saturated air method prior to use. The LDO probe provided comparable results to the Winkler titration ($R^2 = 0.993$, $p < 0.001$, Appendix B), with a more precise DO measurement ($>0.5 \mu\text{mol O}_2 \text{ L}^{-1}$) than the Winkler method ($>2.0 \mu\text{mol O}_2 \text{ L}^{-1}$), and substantially reduced processing time and operating costs.

The difference between the initial and light bottle DO concentration divided by incubation time was used to determine potential net primary production (pNPP) (Eq. 1), while the difference between initial and dark bottle DO concentration divided by incubation time was used to determine RESP (Eq. 2), which are reported as positive values in this paper. Daily potential GPP (pGPP) was calculated as the sum of $\text{pNPP}_{\text{Hourly}}$ and $\text{RESP}_{\text{Hourly}}$ multiplied by the average number of daylight hours (12.13 h) in this study (Eq. 3). Potential MET (pMET) was calculated as the difference between daytime pGPP and daily RESP ($\text{RESP}_{\text{Hourly}}$ multiplied by 24 h) (Eq. 4), under the assumption that phytoplankton RESP is similar under light and dark conditions (Bender et al. 1987).

$$\text{pNPP}_{\text{Hourly}} (\text{mmol O}_2 \text{ m}^{-3} \text{ h}^{-1}) = ([\text{O}_2]_{\text{Light}} - [\text{O}_2]_{\text{Initial}}) / 14 \text{ h} \quad (1)$$

$$\text{RESP}_{\text{Hourly}} (\text{mmol O}_2 \text{ m}^{-3} \text{ h}^{-1}) = ([\text{O}_2]_{\text{Initial}} - [\text{O}_2]_{\text{Dark}}) / 14 \text{ h} \quad (2)$$

$$\text{pGPP}_{\text{Daily}} (\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}) = (\text{pNPP}_{\text{Hourly}} \times \text{daylight hours}) + (\text{RESP}_{\text{Hourly}} \times \text{daylight hours}) \quad (3)$$

$$\text{pMET}_{\text{Daily}} (\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}) = \text{pGPP}_{\text{Daily}} - (\text{RESP}_{\text{Hourly}} \times 24\text{h}) \quad (4)$$

STATISTICAL ANALYSES:

pGPP, RESP, and pMET were compared using individual three-way analysis of variances (ANOVAs) with site (Kiholo Bay vs. Kaloko-Honokohau National Historical Park), plume

(inside vs. outside groundwater plume), and season (wet vs. dry season) as factors. Non-normal data were transformed using an arcsine transformation to meet assumptions for parametric tests. Stepwise linear regression models were used to examine how GPP, RESP, and pMET were related to phytoplankton abundance and biovolume, bacterial abundance, inorganic nutrients and DOM concentrations, and other abiotic factors that influence these biological processes. Correlations were used to examine associations between surface water salinity and nitrate at each site. Statistical analyses were conducted using Minitab 14 statistical software.

RESULTS

SALINITY

Surface water salinity was significantly lower within groundwater plumes ($p < 0.001$), with lower salinity found in-plume at Kiholo Bay (mean $\pm$ SE = 25.81 ± 0.68 ppt) than in-plume at Kaloko-Honokohau National Historical Park (33.85 ± 0.10 ppt). Surface water salinity outside of groundwater plumes were similar at Kiholo Bay (34.64 ± 0.3 ppt) and Kaloko-Honokohau National Historical Park (34.92 ± 0.1 ppt) (Table 1). No significant difference was found in surface water salinity within the groundwater plumes between the wet and dry seasons at Kiholo Bay ($p = 0.495$) or Kaloko-Honokohau National Historical Park ($p = 0.434$).

INCUBATION ANALYSES

GPP

Across sites, average pGPP was over two times higher within groundwater plumes (7.07 ± 2.63 mmol O₂ m⁻³ d⁻¹) than outside of them (2.81 ± 0.24 mmol O₂ m⁻³ d⁻¹) ($p < 0.001$). Overall, pGPP was two times higher at Kiholo Bay (9.51 ± 2.3 mmol O₂ m⁻³ d⁻¹) than at Kaloko-Honokohau National Historical Park (4.85 ± 0.68 mmol O₂ m⁻³ d⁻¹) ($p = 0.015$). pGPP between wet (7.34 ± 1.57 mmol O₂ m⁻³ d⁻¹) and dry (7.61 ± 2.13 mmol O₂ m⁻³ d⁻¹) seasons were similar ($p = 0.319$) across sites. A stepwise linear regression suggests that ESV and DIN were the best predictors of pGPP at Kiholo Bay ($R^2 = 0.52$, $p = 0.004$), while Chl *a* and ESV were the best predictors at Kaloko-Honokohau National Historical Park ($R^2 = 0.71$, $p = 0.008$).

RESP

On average across sites, RESP was two times higher within groundwater plumes (12.39 ± 0.82 mmol O₂ m⁻³ d⁻¹) than outside of them (5.44 ± 0.43 mmol O₂ m⁻³ d⁻¹) ($p < 0.001$). RESP was significantly lower at Kiholo Bay (8.39 ± 0.78 mmol O₂ m⁻³ d⁻¹) than at Kaloko-Honokohau National Historical Park (9.46 ± 0.82 mmol O₂ m⁻³ d⁻¹) ($p = 0.029$). RESP was significantly different between the wet and dry seasons ($p = 0.010$) across sites, with RESP being higher within the dry season (9.80 ± 0.86 mmol O₂ m⁻³ d⁻¹) than during the wet season (7.71 ± 0.68 mmol O₂ m⁻³ d⁻¹). Stepwise linear regressions suggest that NO₃⁻ + NO₂⁻ concentration was the most influential parameter affecting RESP at Kiholo Bay ($R^2 = 39.9\%$, $p < 0.001$), while there were no significant predictors of RESP at Kaloko-Honokohau National Historical Park.

PMET

There was no significant difference in pMET between in-plume and out-plume stations across sites ($p = 0.132$). However, there was a significant difference in MET between sites; surface

waters at Kiholo Bay ($pMET = 1.13 \pm 2.37 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) were less heterotrophic than those at Kaloko-Honokohau National Historical Park ($-4.61 \pm 0.89 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) ($p = 0.003$) (Table 2) (Fig. 4). Surface waters at Kiholo Bay were frequently heterotrophic; however, they switched twice to highly autotrophic during the year. The elevated RESP within the dry season resulted in more heterotrophic conditions in the dry season ($-2.19 \pm 1.50 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) than in the wet season ($-0.36 \pm 2.4 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) across sites ($p = 0.020$). In-plume samples collected at Kiholo Bay during September and November 2011 were major outliers with regards to pGPP and pMET, with measurements eight times and ten times higher than the mean values, respectively. These values were not removed from the data set as they are supported by nutrient and phytoplankton biovolume measurements and represent the high variability within this system. Linear regressions indicated that pGPP ($R^2 = 0.892$, $p < 0.001$) affected pMET more than RESP ($R^2 = 0.099$, $p = 0.002$) at both sites. The two sites were analyzed separately as pGPP, RESP, and pMET were significantly different between sites (Fig. 5). At Kiholo Bay, pGPP explained 89% of the variation in pMET ($p < 0.001$), while RESP only explained 3% ($p = 0.084$). Likewise at Kaloko-Honokohau National Historical Park, pGPP was a significant predictor of pMET ($p = 0.001$) and accounted for 21% of the variability. However at Kaloko-Honokohau National Historical Park, RESP accounted for more of pMET than pGPP, explaining 45% of the variability ($p < 0.001$).

PHYTOPLANKTON BIOVOLUME AND BACTERIAL ABUNDANCE

Phytoplankton biovolume (estimated through ESV) was two times higher within groundwater plumes ($2.66 \times 10^5 \pm 4.39 \times 10^4 \text{ } \mu\text{m}^3 \text{ ml}^{-1}$) than outside of them ($1.10 \times 10^5 \pm 6.52 \times 10^3 \text{ } \mu\text{m}^3 \text{ ml}^{-1}$) ($p < 0.001$). It was also two times higher at Kiholo Bay ($2.30 \times 10^5 \pm 3.86 \times 10^4 \text{ } \mu\text{m}^3 \text{ ml}^{-1}$) than at

Kaloko-Honokohau National Historical Park ($1.31 \times 10^5 \pm 1.29 \times 10^4 \mu\text{m}^3 \text{ ml}^{-1}$) ($p = 0.004$). No difference in phytoplankton biovolume was detected between the wet ($2.02 \times 10^5 \pm 4.20 \times 10^4 \mu\text{m}^3 \text{ ml}^{-1}$) and dry ($1.77 \times 10^5 \pm 2.45 \times 10^4 \mu\text{m}^3 \text{ ml}^{-1}$) seasons ($p = 0.33$) across sites. ESV was significantly correlated to $\text{NO}_3^- + \text{NO}_2^-$ concentrations at Kiholo Bay ($r = 0.41$, $p = 0.001$); however, they were not significantly correlated at Kaloko-Honokohau National Historical Park ($r = 0.30$, $p = 0.057$). Bacteria abundance was significantly higher at Kiholo Bay ($6.51 \times 10^5 \pm 3.5 \times 10^4 \text{ counts ml}^{-1}$) than Kaloko-Honokohau National Historical Park ($5.22 \times 10^5 \pm 1.9 \times 10^4 \text{ counts ml}^{-1}$) ($p = 0.005$). No significant differences in bacterial abundance were found between in- and out-plume stations ($p = 0.219$) or between wet and dry season ($p = 0.994$) across sites (Table 2). Bacteria abundance was significantly correlated to turbidity ($r = -0.424$, $p = 0.003$) and concentrations of TDP ($r = -0.483$, $p < 0.001$), TDN ($r = -0.486$, $p < 0.001$), and DON ($r = -0.445$, $p < 0.001$) at Kiholo Bay; however, was only significantly correlated to DON concentrations ($r = -0.459$, $p = 0.001$) at Kaloko-Honokohau.

DISCUSSION:

EFFECT OF GROUNDWATER ON pGPP, RESP, AND pMET

Increased GPP has been observed in response to freshwater inputs in other tropical (Mead and Wiegner 2010) and temperate (Gazeau et al. 2005; Azevedo et al. 2006) riverine-dominated coastal systems. In this study, mean pGPP was several times higher within groundwater plumes, with measurements as high as $124.0 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$, which was 14 times higher than the maximum pGPP value outside of the groundwater plumes ($8.88 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$). Mixing plots depicting the relationship between surface water salinity and $\text{NO}_3^- + \text{NO}_2^-$ concentrations show

non-conservative mixing at both sites, further suggesting biological uptake of groundwater nutrients (Fig. 3). Increased surface water pGPP within groundwater plumes is likely attributed to utilization of groundwater nutrients by nearshore phytoplankton, as pGPP was positively correlated to phytoplankton biovolume (Fig. 6a) and $\text{NO}_3^- + \text{NO}_2^-$ concentrations (Fig. 6b). Our findings are consistent with previous studies that have found inorganic nutrients, particularly nitrogen, stimulate GPP in coastal (D'Avanzo et al. 1996; Kemp et al. 1997; Caffrey 2004; Azevedo et al. 2006; Russell et al. 2006) and pelagic (MacAndrew et al 2007; Viviani et al. 2011) systems. Concentrations of $\text{NO}_3^- + \text{NO}_2^-$ measured in groundwater entering Kaloko-Honokohau National Historical Park are high (up to $82.6 \mu\text{mol L}^{-1}$) (Knee et al. 2008; Johnson et al. 2008; Street et al. 2008); however, concentrations measured in this study were much lower ($8.36 \pm 1.02 \mu\text{mol L}^{-1}$) within the nearshore groundwater plumes (Table 1). These low $\text{NO}_3^- + \text{NO}_2^-$ concentrations, coupled with PO_4^{3-} concentrations below detection limits suggest that nutrient availability may be limiting GPP.

While low nutrient concentrations may be controlling pGPP at Kaloko-Honokohau National Historical Park, it is difficult to determine what may be controlling productivity at Kiholo Bay. Increased freshwater inputs have been found to negatively influence GPP in tropical river-dominated (Mead and Wiegner et al. 2010) and groundwater-fed (Medina-Gomez and Herrera-Silveira 2006) coastal waters by reducing residence time of nutrients and autotrophs within the system. Residence time at Kiholo Bay is likely small because of the high freshwater discharge rate ($7100 \text{ m}^3 \text{ d}^{-1}$, Peterson et al. 2009) in the nearshore waters. Turbidity also strongly influences GPP in many river-dominated estuaries, where suspended particles reduce light availability to photosynthetic organisms, reducing rates of primary production (Cotner 2000; Pradeep ram et al. 2003; Iriarte et al. 2006; Thottathil et al. 2008). Turbidity at Kiholo Bay was

much lower (0.08 – 0.73 NTU) than that found in river-dominated estuaries in Hawaii (Kaneohe Bay: 1- 8 NTU, De Carlo et al. 2007; Hilo Bay: 0.7 - 6.8 NTU, Mead and Wiegner 2010). While high turbidity may not be inflicting light limitation, photosynthesis vs irradiance curves for each site (Appendix A) suggest that high *in situ* light intensity (as high as 2025 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$) may lead to photoinhibition, where primary productivity is reduced.

RESP in river-dominated estuaries has been found to increase in response to increased freshwater inputs in some regions (Pradeep Ram et al. 2003; Russell et al. 2006) and decrease in others (Mead and Wiegner 2010). This study found RESP was significantly higher within groundwater plumes, suggesting that groundwater inputs stimulated heterotrophic processes. RESP increases are typically attributed to high organic matter inputs (Smith and Hollibaugh 1993; Kemp et al. 1997; Gazeau et al. 2005), while decreases in RESP may be due to flushing and displacement of autotrophs and heterotrophs (Iriarte et al. 1996; Mead and Wiegner 2010). Our study found no strong associations between RESP and DOC, DON, or DOP concentrations at both sites; however, concentrations may not be representative organic matter loading as cycling efficiency can be high within the microbial loop (Azam et al. 1994). RESP has also been shown to be positively correlated to Chl *a* in a temperate riverine estuary at concentrations above 5 $\mu\text{g L}^{-1}$ (Iriarte et al. 1996). The sites sampled in this study are oligotrophic, with low Chl *a* concentrations (range = 0.01 - 2.57 $\mu\text{g L}^{-1}$), which may explain why no relationship was found between Chl *a* and RESP. Bacterial abundance has also been found to be significantly correlated to RESP (Iriarte et al. 1996); however, it was not in our study, which may be explained by the low bacterial abundances measured at Kiholo Bay and Kaloko-Honokohau National Historical Park ($2.4 \times 10^5 - 1.4 \times 10^6 \text{ cells ml}^{-1}$). While $\text{NO}_3^- + \text{NO}_2^-$ concentrations were found to strongly influenced RESP at Kiholo Bay, the driving force of RESP at Kaloko-Honokohau remains

unclear. Kaloko Fishpond is a highly productive (Bulsecu et al., unpub. data), coastal brackish pond that enters the nearshore waters at Kaloko-Honokohau National Historical Park through a small inlet. The microbial community and organic matter that enters the relatively nutrient-poor coastal waters from Kaloko Fishpond may be enhancing RESP along with the resident microbial community.

Trophic conditions have been shown to vary both within and between systems, with net heterotrophy dominating the majority of tropical (Pradeep Ram et al. 2003; Thottathil et al. 2008) and temperate river-dominated estuaries studied to date (Smith and Hollibaugh 1993; Caffrey 2004; Gazeau et al. 2005; Delgadillo-Hinojosa et al. 2008); however, autotrophic conditions have been found in coastal Hawaiian waters (Ringuelet and Mackenzie 2005; Mead and Wiegner 2010). When in-plume data from both sites were combined and compared to out-plume data, no significant differences in pMET were observed. However, significant pMET responses to groundwater inputs become more apparent when examining sites individually (Fig. 4). At Kiholo Bay, in-plume pGPP exceeded RESP, resulting in net autotrophic conditions. In contrast, at Kaloko-Honokohau National Historical Park in-plume RESP exceeded pGPP, resulting in net heterotrophic conditions. MET and the trophic status of an estuary depends on the many factors that can influence GPP and RESP. Previous research has suggested that the ratio of DIN to organic matter loading may control MET (Kemp et al. 1997); however, loading was not measured in this study. While the response within the groundwater plumes varied between sites, the out-plume regions were less variable, with net heterotrophic conditions prevailing. Similarly, oceanic ends of estuaries are generally less variable than their freshwater ends, as they receive less terrestrial derived nutrients and organic matter than their freshwater ends (Caffrey 2004;

Gazeau et al. 2005; Azevedo et al. 2006). Open ocean MET measurements are also much less variable and typically near balance (Smith and Hollibaugh 1993; Viviani et al. 2011).

COUPLING BETWEEN PROCESSES

Coupling between production and consumption of organic matter can be used to infer trophic efficiency. In tightly coupled, more efficient systems, changes in RESP generally coincide with changes in GPP, as RESP is dependent on *in situ* production (Smith and Kemp 1995).

Decoupling of these processes and low trophic efficiency can occur as allochthonous organic matter enters a system, increasing RESP, or as autochthonous organic matter exits, reducing RESP. Coupling between pGPP and RESP was weak at our sites, with only 1.2% of RESP explained by pGPP at Kiholo Bay ($p = 0.413$) and 9.9% at Kaloko-Honokohau National Historical Park ($p = 0.033$) (Fig. 5). Previous studies have suggested that coupling between GPP and RESP may vary as a function of productivity, where in highly autotrophic waters GPP and RESP are poorly coupled, while in highly heterotrophic waters coupling between GPP and RESP can be high (Biddanda et al. 1994; Smith and Kemp 1995; Iriarte et al. 1996). While most samples collected in this study exhibited relatively low productivity, decoupling of pGPP and RESP was most apparent in the samples with high pGPP (Fig. 5). The absence of strong coupling shows that RESP was largely independent of pGPP, suggesting that RESP may be supported by allochthonous organic matter from groundwater inputs.

GPP and RESP can both be significant predictors of pMET. Our findings show that pGPP strongly affected pMET at Kiholo Bay, explaining 89.2% of the variation in pMET, while RESP explained only 3% of pMET ($p = 0.084$). Our study suggests that pGPP was stimulated by $\text{NO}_3^- + \text{NO}_2^-$ concentrations at Kiholo Bay, which supports previous research that has found that

positive MET estuaries are strongly influenced by nutrients (Kemp et al. 1997; Russell et al. 2006; Delgadillo-Hinojosa et al. 2008). Nutrient concentrations in the nearshore waters of Kaloko-Honokohau National Historical Park were low (Table 1), suggesting that high nutrient concentrations found within groundwater may be consumed by nearshore regions, such as the highly productive Kaloko Fishpond (Bulsecu et al., unpub. data). These low nutrient concentrations may be responsible for pGPP exerting less influence on pMET ($R^2 = 0.229$, $p = 0.001$), enabling RESP to influence pMET to a larger extent ($R^2 = 0.466$, $p < 0.001$).

TEMPORAL AND SPATIAL VARIABILITY

In order to properly assess trophic conditions of a system, temporal and spatial variability must be taken into account. Seasonal variations of MET are found in many coastal systems, where light intensity, day length, water temperature, and other factors that influence GPP and RESP vary temporally. Since seasonal variability increases with latitude, seasonal effects are likely to be higher in temperate regions than in tropical ones. A comprehensive study examining net ecosystem MET in 22 estuaries throughout North America noted that seasonal variations were relatively low in the Caribbean and Gulf of Mexico estuaries compared to more temperate US estuaries, concluding that temperature was more influential than inorganic nutrient concentrations on MET (Caffrey 2004). The incubation method used in this study controlled light and temperature conditions to focus on the impact of groundwater inputs, so seasonal variations measured here can be attributed to changes in inorganic nutrient and organic matter concentrations, as well as variability of phytoplankton and bacterioplankton communities. Studies have found increases in both GPP and RESP during summer; however, systems typically become more heterotrophic during the dry summer months (Kemp and Boynton 1992; Smith and

Hollibaugh 1997; Duarte et al. 2004; Hashimoto et al. 2006). While we did not find a seasonal response in pGPP, RESP was significantly higher within dry seasons, resulting in more heterotrophic conditions (Fig. 4). Other studies have found a reduction in GPP during wet seasons, as increased freshwater inputs can reduce residence time and flush autotrophs from the system (Medina-Gomez and Herrera-Silveira 2006; Mead and Wiegner 2011). While we did not find seasonal differences in pGPP, displacement of microbes or a decrease in residence time may be shifting the geographic extent of the biological response outside of the in-plume region we studied. In our study, variability of pGPP and PMET was profound on shorter temporal scales, with large month to month variability that did not fall within a particular season. At Kiholo Bay, high pGPP was observed in September 2011 ($54.7 \pm 34.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$) and November 2011 ($42.3 \pm 10.6 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$), whereas it was relatively low in October 2011 ($6.44 \pm 1.31 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$). These pulses in GPP, and those found in other studies (Karl et al. 2003) suggest that MET measurements in highly dynamic systems should be taken on short temporal scales in order to accurately assess the metabolic condition of a system and its true contribution to the global carbon cycle.

High spatial variability in MET has been found in many systems (Smith and Kemp 2001; Russell et al. 2006; Russell and Montagna 2007; Mead and Wiegner 2010), but not in all (Caffrey 2003; D'Avanzo et al. 1996). High spatial variability in GPP, RESP, and MET were found both between and within sites on the leeward sides of Hawaii Island. Kiholo Bay and Kaloko-Honokohau National Historical Park are both groundwater-fed systems only 25 km apart; however, they had contrasting metabolic conditions. Within sites, pGPP, RESP, and pMET varied considerably between in- and out-plume regions, only 0.5 km apart (Fig. 4). High variability was also found at much smaller spatial scales within the groundwater plume region.

The largest variation was found at Kiholo Bay in September 2011, where in-plume pGPP varied from 17.0 to 124.0 mmol O₂ m⁻³ d⁻¹ in samples collected only 20 m apart. Understanding spatial variability within a system is crucial in formulating broad-reaching conclusions from geographically isolated measurements.

CONCLUSION

This study has shown that groundwater inputs stimulate biological processes within the coastal surface-water microbial community. Groundwater nutrients and organic matter inputs led to increased pGPP and RESP; however, the magnitude of response of these parameters varied between sites, resulting in contrasting pMET conditions. Understanding the response of coastal waters to groundwater discharge has become increasingly important in leeward Hawaii Island as increasing development, invasive flora, and climate change are projected to degrade the quality and quantity of coastal groundwater inputs. This study also has broader implications elsewhere as global carbon models largely dismiss the coastal ocean due to its relatively small geographic area and highly dynamic and poorly understood carbon contribution (Smith and Hollibaugh 1993). The high temporal and spatial variability found in this study and many others (e.g. Smith and Hollibaugh 1993, 1997; Smith and Kemp 1997; Caffrey 2004) reveal the importance of using repeated measures over short spatial and temporal scales to properly extrapolate to a global scale.

REFERENCES

- Azam, F., Smith, D.C., Steward, G.F., and Å. Hagström. 1994. Bacteria-organic matter coupling and its significance for oceanic carbon cycling. *Microbial Ecology* 28:167-179
- Azevedo, I.C., Duarte, P.M., and A.A. Bordalo. 2006. Pelagic metabolism of the Douro estuary (Portugal) – Factors controlling primary production. *Estuarine, Coastal and Shelf Science* 69:133-146
- Bean, B.W., Stankelis, R.M., Lawrence, J.M., and W.R. Boynton. 2002. High Resolution Mapping of Surface Waters. Ecosystem processes component Level 1 interpretative report No. 19. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. [UMCEES] CBL Ref. No. 02-0152a
- Bender, M., K. Grande, K. Johnson, J. Marra, P.J.L. Williams, J. Sieburth, M. Pilson, C. Langdon, G. Hitchcock, J. Orcha rdo, C. Hunt, P. Donaghay, and K. Heinemann. 1987. A comparison of four methods for determining planktonic community production. *Limnology and Oceanography* 32:1085-1098.
- Biddanda, B., S. Opsahl, and R. Benner. 1994. Plankton respiration and carbon flux through bacterioplankton on the Louisiana shelf. *Limnology and Oceanography* 39:1259-1275.
- Caffrey, J. M. 2003. Production, respiration, and net ecosystem metabolism in U.S. estuaries. *Environmental Monitoring and Assessment* 81:207-219
- Caffrey, J.M. 2004. Factors controlling net ecosystem metabolism in U.S. estuaries. *Estuaries and Coasts* 27:90-101
- Caffrey, J. M., T. P. Chapin, H. W. Jannasch, and J. C. Haskins. 2007. High nutrient pulses, tidal mixing and biological response in a small California estuary: Variability in nutrient concentrations from decadal to hourly time scales. *Estuarine, Coastal and Shelf Science* 71:368-380
- Cotner, J. B., Johengen, T. H., and B. A. Biddanda. 2000. Intense winter heterotrophic production stimulated by benthic resuspension. *Limnology and Oceanography* 45:1672-1676
- D'Avanzo, D. C., J. N. Kremer, and S. C. Wainright. 1996. Ecosystem production and respiration in response to eutrophication in shallow temperate estuaries. *Marine Ecology Progress Series* 141:263-274
- De Carlo, E.H., D.J. Hoover, C.W. Young, R.S. Hoover, and F.T. Mackenzie. 2007. Impact of storm runoff from tropical watersheds on coastal water quality and productivity. *Applied Geochemistry* 22:1777-1797.

- Delgadillo-Hinojosa, F., A. Zirino, O. Holm-Hansen, J. M. Hernández-Ayón, T. J. Boyd, B. Chadwick, and I. Rivera-Duarte. 2008. Dissolved nutrient balance and net ecosystem metabolism in a Mediterranean-climate coastal lagoon: San Diego Bay. *Estuarine, Coastal and Shelf Science* 76:594-607
- DeVerse, K. 2006. Appendix A: Kaloko-Honokohau National Historical Park resource overview. In: HaySmith, L., F. L. Klasner, S. H. Stephens, and G. H. Dicus. Pacific Island Network vital signs monitoring plan. Natural Resource Report NPS/PACN/NRR—2006/003 National Park Service, Fort Collins, Colorado.
- Duarte, C.M., and S. Agustí. 1998. The CO₂ balance of unproductive aquatic ecosystems. *Science* 281: 234-236.
- Duarte, C.M., S. Agustí, and D. Vaquè. 2004. Controls on planktonic metabolism in the Bay of Blanes, northwestern Mediterranean littoral. *Limnology and Oceanography* 49:2162-2170.
- Eyre, B.D. and L.J. McKee. 2002. Carbon, nitrogen, and phosphorus budgets for a shallow subtropical coastal embayment (Moreton Bay, Australia). *Limnology and Oceanography* 47:1043–1055
- Fuhrman, J. (2000). Impact of viruses on bacterial processes. In D. L. Kirchmann (Ed.), *Microbial Ecology of the Oceans* (pp. 327–350). New York: John Wiley and Sons, Inc
- Garrison, G. H., C. R. Glenn, and G. M. McMurtry. 2003. Measurement of submarine groundwater discharge in Kahana Bay, Oahu, Hawaii. *Limnology and Oceanography* 48:920-928
- Gazeau, F., Gattuso, J-P., Middelburg, J.J, Brion, N., Schietyecatíe, L-S., Frankignoulle, M., and A.V. Borges. 2005. Planktonic and whole system metabolism in a nutrient-rich estuary (the Scheldt Estuary). *Estuaries* 28:868-883
- Gobler, C. J., and S. A. Sañudo-Wilhelmy. 2001. Temporal variability of groundwater seepage and brown tide blooms in a Long Island embayment. *Marine Ecology Progress Series* 217:299–309
- Hashimoto, S., Horimoto, N., Ishimaru, T., and T. Saino. 2006. Metabolic balance of gross primary production and community respiration in Sagami Bay, Japan. *Marine Ecology Progress Series* 321:31–40
- Hu, C. Muller-Karger, F. E., and P. W. Swarzenski. 2006. Hurricanes, submarine groundwater discharge, and Florida's red tides. *Geophysical Research Letters* 33:L11601-L11603

- Hwang, D., Y. Lee, and G. Kim 2005. Large submarine groundwater discharge and benthic eutrophication in Bangdu Bay on volcanic Jeju Island, Korea. *Limnology and Oceanography*. 50:1393–1403
- Iriarte, A., I. De Madariaga, F. Diez-Garagarza, M. Revilla, and E. Orive. 1996. Primary plankton production, respiration and nitrification in a shallow temperate estuary during summer. *Journal of Experimental Marine Biology and Ecology*. 208:127-151
- Johnson, A. G., C. R. Glenn, W. C. Burnett, R. N. Peterson, and P. G. Lucey. 2008. Aerial infrared imaging reveals large nutrient-rich groundwater inputs to the ocean. *Geophysical Research Letters*. 35
- Kemp, W. M. and W. R. Boynton. 1992. Benthic-pelagic interactions: Nutrients and oxygen dynamics, p. 149–209. in D. E. Smith, M. Leffler, and G. Mackiernan (eds.), *Oxygen Dynamics in the Chesapeake Bay—A Synthesis of Recent Results*. A Maryland Sea Grant Book, College Park, Maryland
- Kemp, W. M., E. M. Smith, M. Marvin-DiPasquale, and W. R. Boynton. 1997. Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. *Marine Ecology Progress Series* 150:229-248
- Knee, K., J. Street, E. Grossman, A. Paytan. 2008. Submarine ground-water discharge and fate along the coast of Kaloko-Honokohau national historical park, Island of Hawaii part 2, spatial and temporal variations in salinity, radium-isotope activity, and nutrient concentrations in coastal waters, December 2003–April 2006 USGS
- Li, W., Zohary, T., Yacobi, Y., and A.M. Wood. 1993. Ultraphytoplankton in the eastern Mediterranean sea: towards deriving phytoplankton biomass from flow cytometric measurements of abundance, fluorescence and light scatter. *Marine Ecology Progress Series* 19:79-87
- McAndrew, P.M., Björkman, K.M., Church, M.J., Morris, P.J., Jachowski, N., Williams, P.J. le B. and Karl, D.M. 2007. Metabolic response of oligotrophic plankton communities to deep water nutrient enrichment. *Marine Ecology Progress Series* 332:30-75.
- Mead, L. H., and T. Wiegner. 2010. Surface water metabolism potential in a tropical estuary, Hilo Bay, Hawai'i, USA, during storm and non-storm conditions. *Estuaries and Coasts* 33:1099-1112
- Medina-Gómez, I., and J. A. Herrera-Silveira. 2006. Primary production dynamics in a pristine groundwater influenced coastal lagoon of the Yucatan Peninsula. *Continental Shelf Research* 26:971-986
- Oki, D. S. 1999. Geohydrology and numerical simulation of the ground-water flow system of Kona, Island of Hawaii, U.S. Geological Survey Water-Resources Investigations Report 99-4070

- Paytan, A., G. G. Shellenbarger, J. Street, M. E. Gonneea, K. Davis, M. B. Young, and W. S. Moore. 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. *Limnology and Oceanography* 51:343-34
- Peterson, R. N., W. C. Burnett, C. R. Glenn, and A. G. Johnson 2009. Quantification of point-source groundwater discharges to the ocean from the shoreline of the Big Island, Hawai'i. *Limnology and Oceanography* 54:890-904
- Pradeep Ram, A. S., S. Nair, and D. Chandramohan. 2003. Seasonal shift in net ecosystem production in a tropical estuary. *Limnology and Oceanography* 48:1601-1607
- Ringuet, S. and F.T. Mackenzie. 2005. Controls on nutrient and phytoplankton dynamics during normal flow and storm runoff conditions, southern Kane'ōhe Bay, Hawaii. *Estuaries* 28:327-337.
- Russell, M.J., Montagna, P.A., and R.D. Kalke. 2006. The effect of freshwater inflow on net ecosystem metabolism in Lavaca Bay, Texas. *Estuarine, Coastal and Shelf Science*. 68:231-244
- Russell, M.J. and P.A. Montagna. 2007. Spatial and temporal variability and drivers of net ecosystem metabolism in western Gulf of Mexico estuaries. *Estuaries and Coasts* 30:137-153.
- Sharp, S. H., et al. 2002. A preliminary method comparison for measurement of dissolved organic nitrogen in seawater. *Marine Chemistry* 78: 171-184
- Slomp, C. P., and P. Van Cappellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* 295:64-86
- Smith, C. M. and J. E. Smith, C. M. 2006, Algal blooms in north Kihei: an assessment of patterns & processes relating nutrient dynamics to algal abundance: Report to City and County of Maui, University of Hawaii at Manoa, Hawaii.
- Smith, E.M., and W.M. Kemp. 1995. Seasonal and regional variations in plankton community production and respiration for Chesapeake Bay. *Marine Ecology Progress Series* 116: 217-231.
- Smith, E.M. and W.M. Kemp. 2001. Size structure and the production/respiration balance in a coastal plankton community. *Limnology and Oceanography* 46:473-485
- Smith, S. V., and J. T. Hollibaugh. 1993. Coastal metabolism and the oceanic organic carbon balance. *Review of Geophysics*. 31:75-89

- Smith, S. V., and J. T. Hollibaugh. 1997. Annual cycle and interannual variability of ecosystem metabolism in a temperate climate embayment. *Ecological Monographs* 67:509-533
- Street, J. H., K. L. Knee, E. E. Grossman, and A. Paytan. 2008. Submarine groundwater discharge and nutrient addition to the coastal zone and coral reefs of leeward Hawai'i. *Marine Chemistry* 109:355-376
- Thottathil, S. D., K. K. Balachandran, G. V. M. Gupta, N. V. Madhu, and S. Nair. 2008. Influence of allochthonous input on autotrophic-heterotrophic switch-over in shallow waters of a tropical estuary (Cochin Estuary), India. *Estuarine, Coastal and Shelf Science* 78:551-562
- Umezawa, Y., T. Miyajima, H. Kayanne, and I. Koike. 2002. Significance of groundwater nitrogen discharge into coral reefs at Ishigaki Island, southwest of Japan. *Coral Reefs* 21:346-356
- Van Beukering, P. F. H., and H. S. F. Cesar. 2004. Ecological economic modeling of coral reefs: evaluating tourist overuse at Hanauma Bay and algal blooms at the Kihei Coast, Hawai'i. *Pacific Science* 58:243-260
- Viviani, D. A., K. M. Björkman, D. M. Karl, and M. J. Church, 2011. Plankton metabolism in surface waters of the tropical and subtropical Pacific Ocean. *Aquatic Microbial Ecology* 62: 1-12

Table 1. Mean (SE) physiochemical and nutrient parameters of surface water samples collected at Kiholo Bay and Kaloko-Honokohau National Historical Park, Hawaii, USA. Measurements of dissolved organic phosphorous were below detection limits of 0.5 $\mu\text{mol L}^{-1}$.

Site	Location	Season	Temp ($^{\circ}\text{C}$)	Salinity (ppt)	pH	Turbidity (NTU)	PO_4^{3-} ($\mu\text{mol L}^{-1}$)	$\text{NO}_3^- + \text{NO}_2^-$ ($\mu\text{mol L}^{-1}$)	DIN ($\mu\text{mol L}^{-1}$)	DON ($\mu\text{mol L}^{-1}$)	DOC ($\mu\text{mol L}^{-1}$)
Kiholo Bay	in-plume	wet	25.0 (0.2)	25.3 (0.9)	8.13 (0.03)	0.36 (0.09)	0.48 (0.16)	15.99 (1.78)	16.55 (1.83)	25.46 (11.86)	138.02 (35.68)
		dry	25.4 (0.1)	26.2 (1.0)	8.10 (0.01)	0.37 (0.04)	0.25 (0.07)	11.75 (1.48)	12.89 (1.46)	10.34 (2.54)	202.65 (21.97)
	out-plume	wet	25.0 (0.1)	34.0 (0.5)	8.14 (0.01)	0.20 (0.04)	0.01 (0.01)	2.64 (0.76)	4.50 (0.88)	26.47 (11.14)	145.77 (39.12)
		dry	25.78 (0.1)	35.1 (0.1)	8.14 (0.02)	0.16 (0.01)	0.09 (0.06)	0.85 (0.24)	4.24 (0.78)	6.62 (1.74)	253.10 (51.86)
Kaloko-Honokohau	in-plume	wet	24.1 (0.2)	33.8 (0.2)	8.24 (0.02)	0.32 (0.11)	ND < 0.1	2.65 (0.29)	4.81 (0.82)	28.96 (12.65)	172.37 (47.64)
		dry	25.9 (0.1)	33.9 (0.1)	8.26 (0.02)	0.24 (0.03)	ND < 0.1	1.35 (0.10)	5.51 (0.67)	5.80 (1.38)	220.31 (38.57)
	out-plume	wet	24.1 (0.3)	35.1 (0.2)	8.20 (0.01)	0.23 (0.07)	ND < 0.1	0.97 (0.19)	2.69 (0.70)	37.30 (17.68)	185.65 (46.39)
		dry	25.9 (0.1)	34.7 (0.1)	8.20 (0.02)	0.13 (0.01)	ND < 0.1	1.12 (0.19)	5.58 (0.65)	5.92 (1.48)	214.11 (28.80)

Table 2. Mean (SE) biological parameters of surface water samples collected at Kiholo Bay and Kaloko-Honokohau National Historical Park, Hawaii Island, USA.

Site	Location	Season	pGPP (mmol O ₂ m ⁻³ d ⁻¹)	RESP (mmol O ₂ m ⁻³ d ⁻¹)	pMET (mmol O ₂ m ⁻³ d ⁻¹)	Bacteria abundance (x10 ⁵ cells ml ⁻¹)	Phytoplankton abundance (x10 ³ cells ml ⁻¹)	Phytoplankton Biovolume (x10 ⁵ μm ³ ml ⁻¹)	Chl <i>a</i> (μg L ⁻¹)
Kiholo Bay	in-plume	wet	14.32 (5.41)	11.53 (1.19)	2.79 (5.44)	6.81 (1.01)	6.14 (0.81)	4.50 (1.45)	0.48 (0.08)
		dry	16.68 (6.45)	12.88 (1.61)	3.80 (7.07)	7.46 (0.83)	16.25 (2.83)	2.69 (0.65)	0.30 (0.05)
	out-plume	wet	3.73 (0.74)	3.93 (0.88)	-0.21 (1.23)	5.49 (0.34)	8.84 (1.50)	1.15 (0.20)	0.17 (0.05)
		dry	3.00 (0.26)	4.76 (0.65)	-1.76 (0.57)	6.01 (0.29)	22.92 (2.27)	1.17 (0.07)	0.10 (0.01)
Kaloko- Honokohau	in-plume	wet	9.13 (1.96)	10.61 (1.02)	-1.48 (2.27)	5.53 (0.38)	7.46 (0.79)	1.57 (0.31)	0.99 (0.28)
		dry	4.59 (0.93)	14.66 (2.53)	-10.07 (2.06)	4.02 (0.23)	13.13 (2.32)	1.63 (0.36)	0.28 (0.04)
	out-plume	wet	2.20 (0.46)	4.75 (0.75)	-2.56 (0.75)	5.62 (0.39)	8.55 (1.16)	0.88 (0.10)	0.27 (0.07)
		dry	3.43 (0.44)	8.68 (0.63)	-5.25 (0.41)	5.46 (0.24)	13.38 (1.39)	1.21 (0.17)	0.18 (0.03)

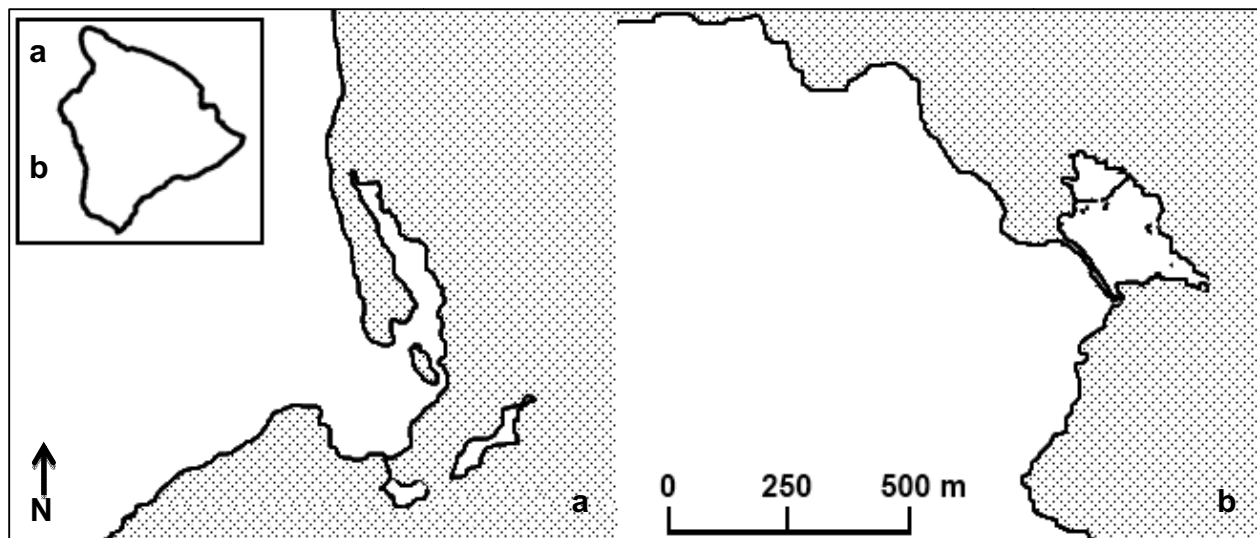


Figure 1. Kiholo Bay (a) and Kaloko-Honokohau (b) are two nearshore regions on the leeward coast of Hawaii Island (inset), USA where groundwater enters the coastal ocean.

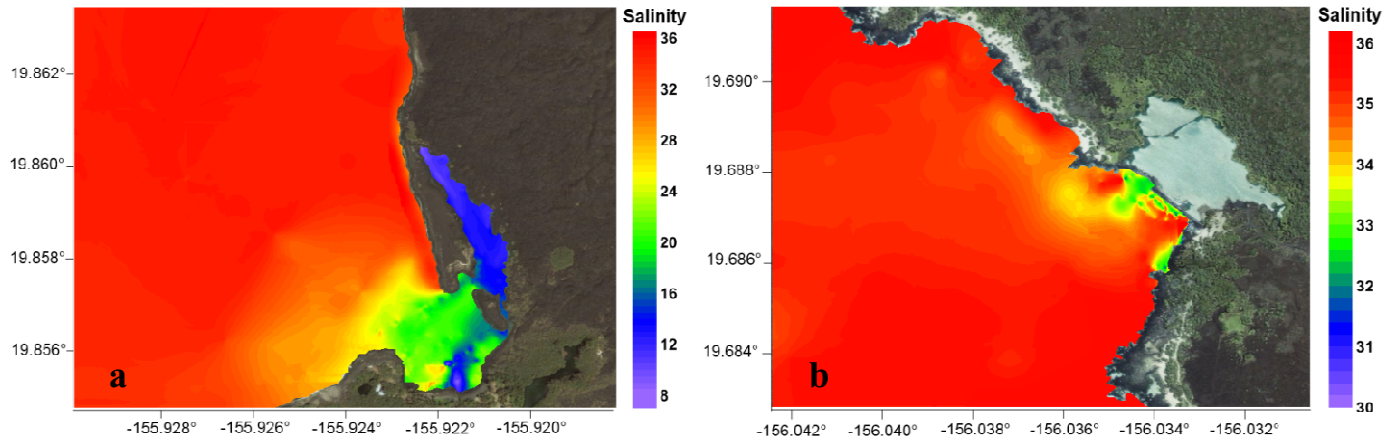


Figure 2. Surface water salinity mapping was used to delineate regions inside and outside of groundwater plumes on each sampling day. Above maps are examples of maps developed at Kiholo Bay (a) on October 23, 2011 and Kaloko-Honokohau (b), Hawaii Island, USA, on July 29, 2011.

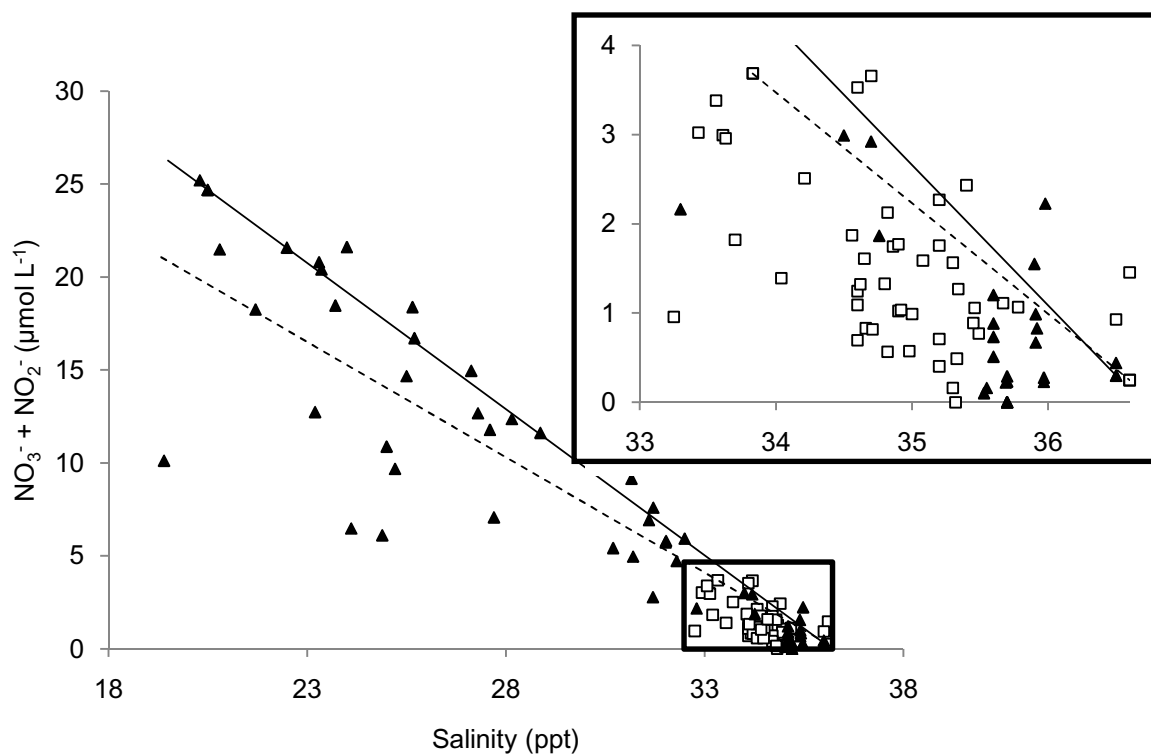


Figure 3. Mixing plot of $\text{NO}_3^- + \text{NO}_2^-$ concentrations with salinity. Triangles represent samples collected at Kiholo Bay (solid conservative mixing line) while squares represent samples collected at Kaloko-Honokohau (dashed conservative mixing line). The enclosed area is an enlargement of the values found at higher salinities

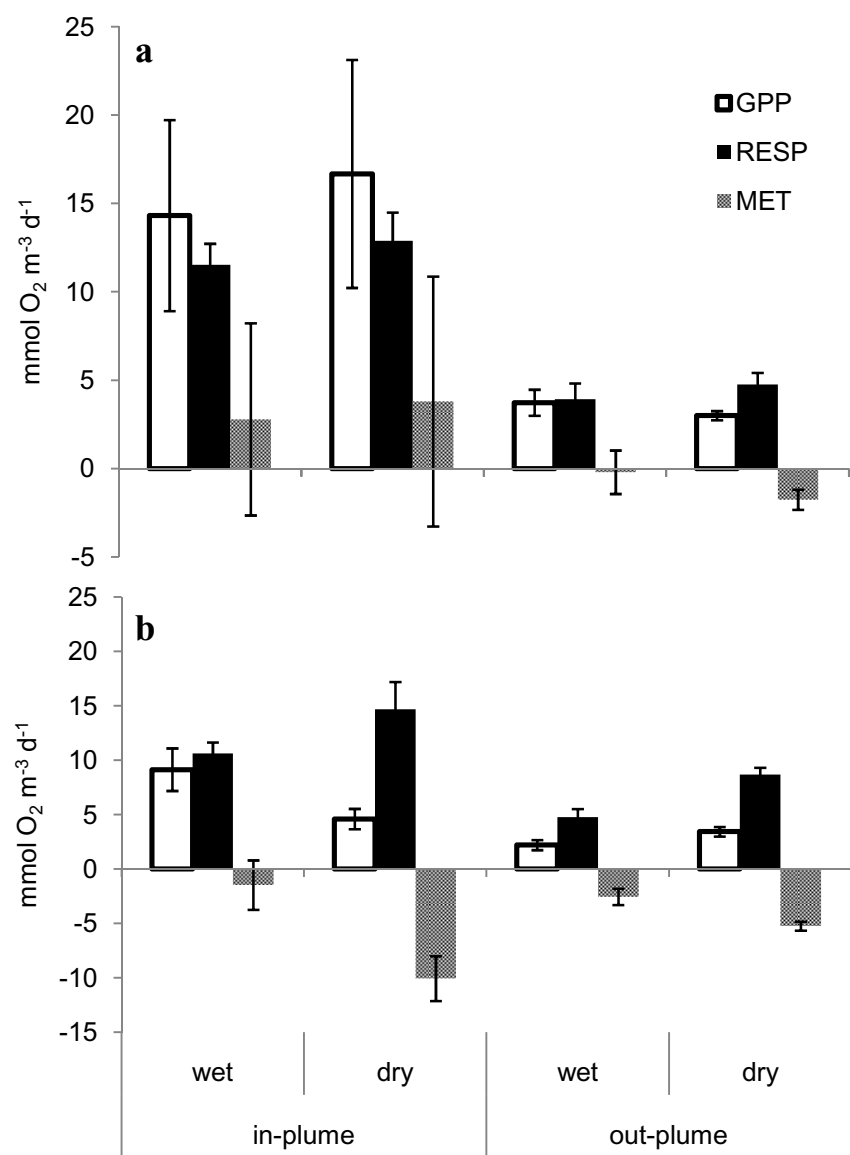


Figure 4. Average (SE) pGPP, RESP, and pMET at Kiholo Bay (a) and Kaloko-Honokohau (b), Hawaii USA, observed inside and outside for groundwater plumes during wet and dry seasons (2011-2012).

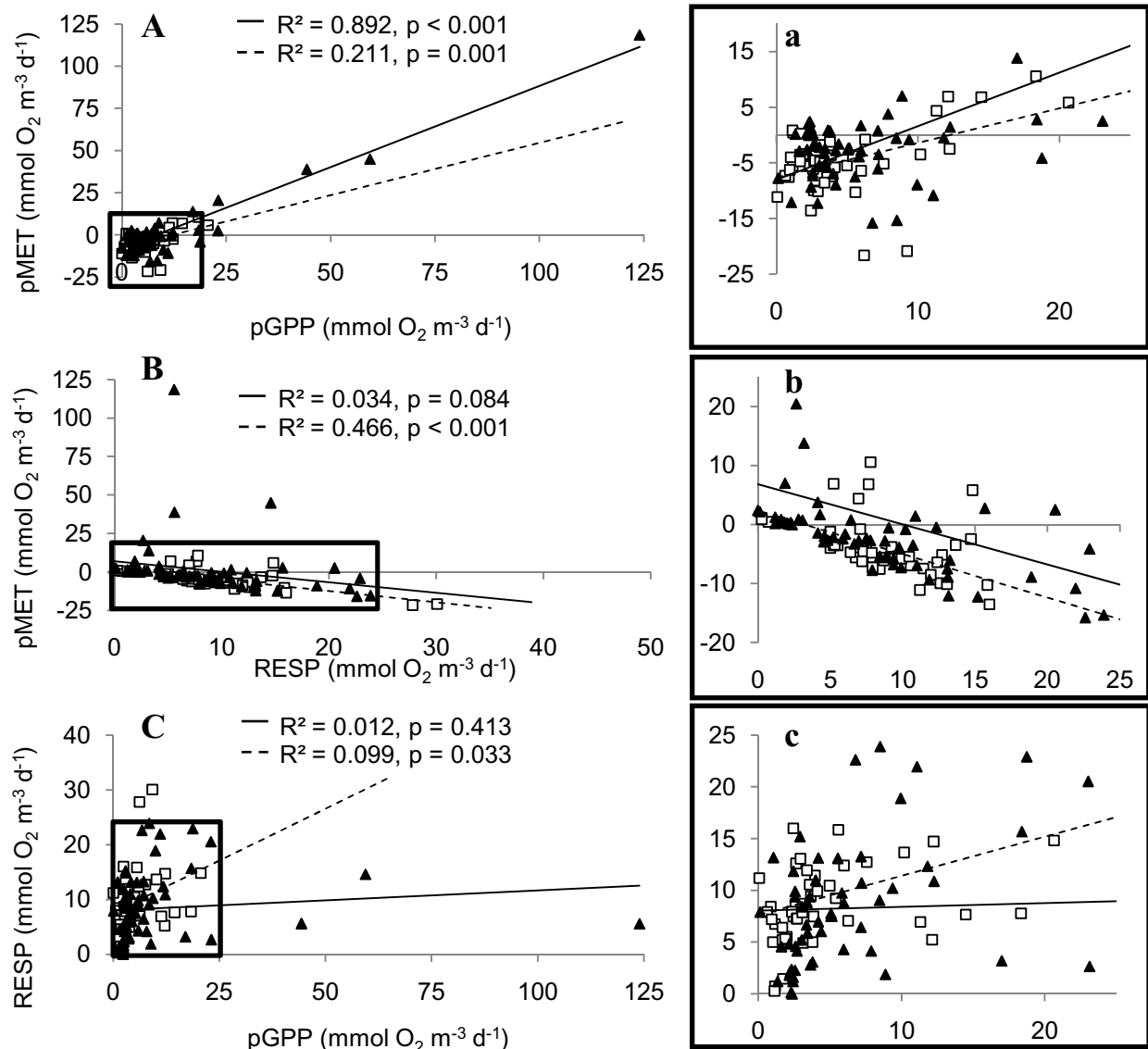


Figure 5. Regression analyses examine the influence of pGPP on pMET (A,a), RESP on pMET (B,b), and pGPP on RESP (C,c) in surface water samples. Triangles represent data collected at Kiholo Bay (solid trendline). Squares represent data collected at Kaloko-Honokohau (dashed trendline), Hawaii Island, USA. Enclosed areas are enlargement of values found at the low-end of the scale.

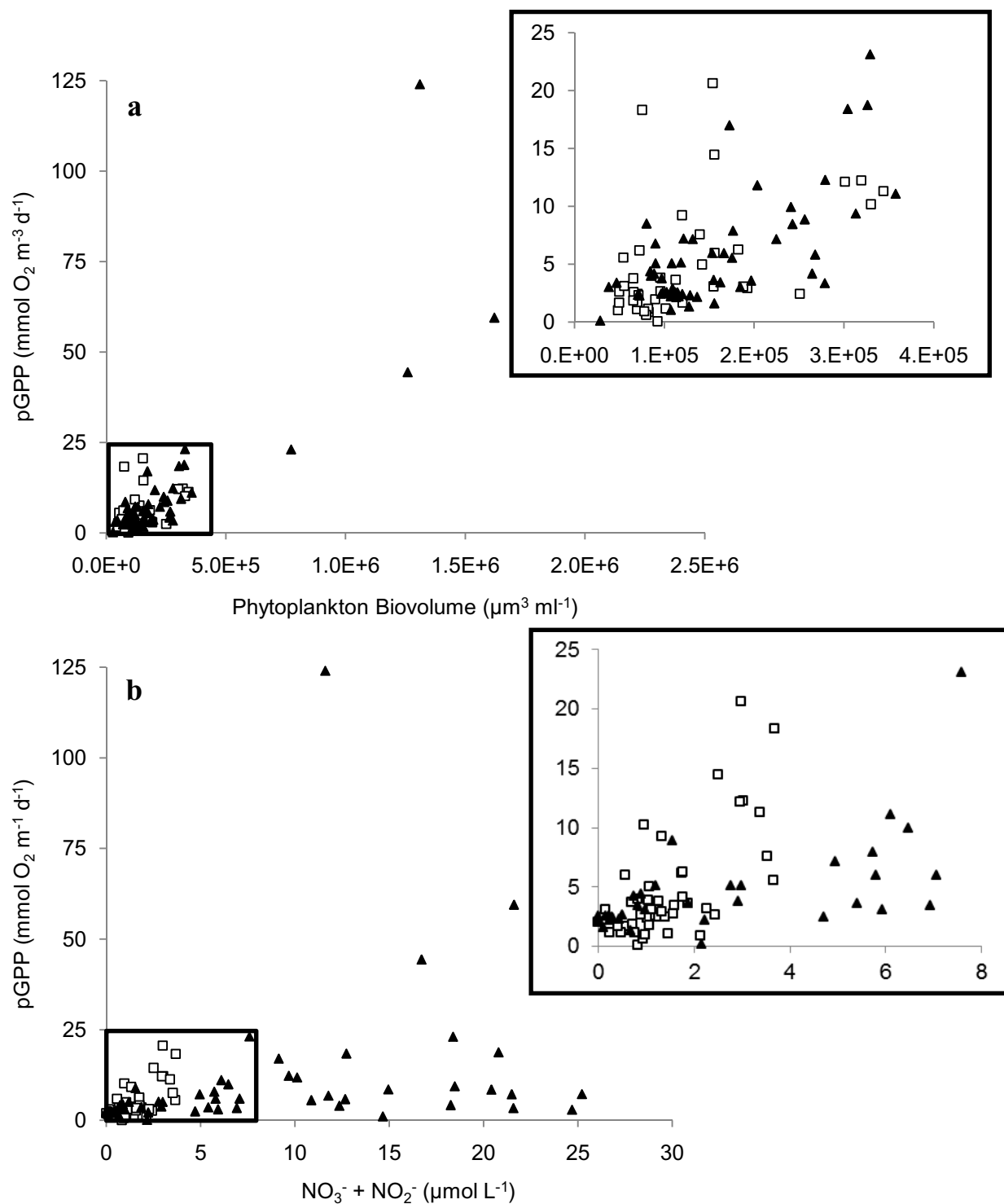
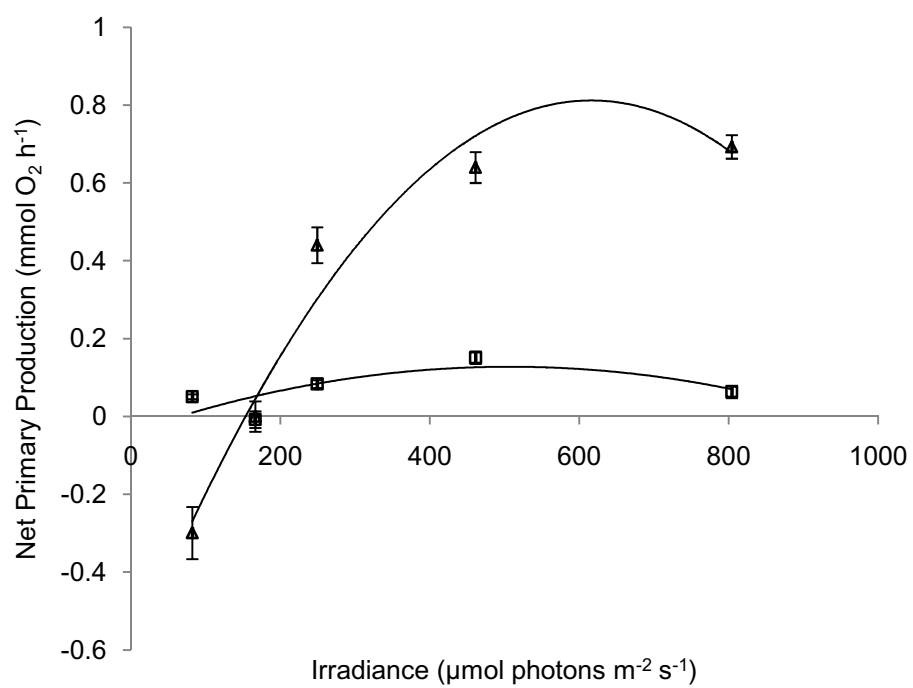


Figure 6. pGPP was significantly correlated to phytoplankton biovolume (a) at Kiholo Bay (triangles) ($r = 0.679$, $p < 0.001$), and Kaloko-Honokohau (squares) ($r = 0.545$, $p < 0.001$) and to NO₃⁻ + NO₂⁻ concentrations (b) at Kiholo Bay (triangles) ($r = 0.527$, $p < 0.001$), and Kaloko-Honokohau (squares) ($r = 0.627$, $p < 0.001$), Hawaii Island, USA. Enclosed areas are enlargement of values clustering around the low ends of the axes

Appendix A: Photosynthesis (average NPP $\pm$ SE) versus Irradiance curves for surface waters collected at Kiholo Bay (triangles) and Kaloko-Honokohau (squares), Hawaii Island, USA, in February 2011.



Appendix B: The relationship between DO measurements made using the Hach LBOD101 luminescence dissolved oxygen probe and the azide modified Winkler titration method (SM 4500-O C). Results from a regression analysis are shown on the figure ($\alpha = 0.05$)

